

# STM/LEEM study of film growth of pentacene and pentacenequinone

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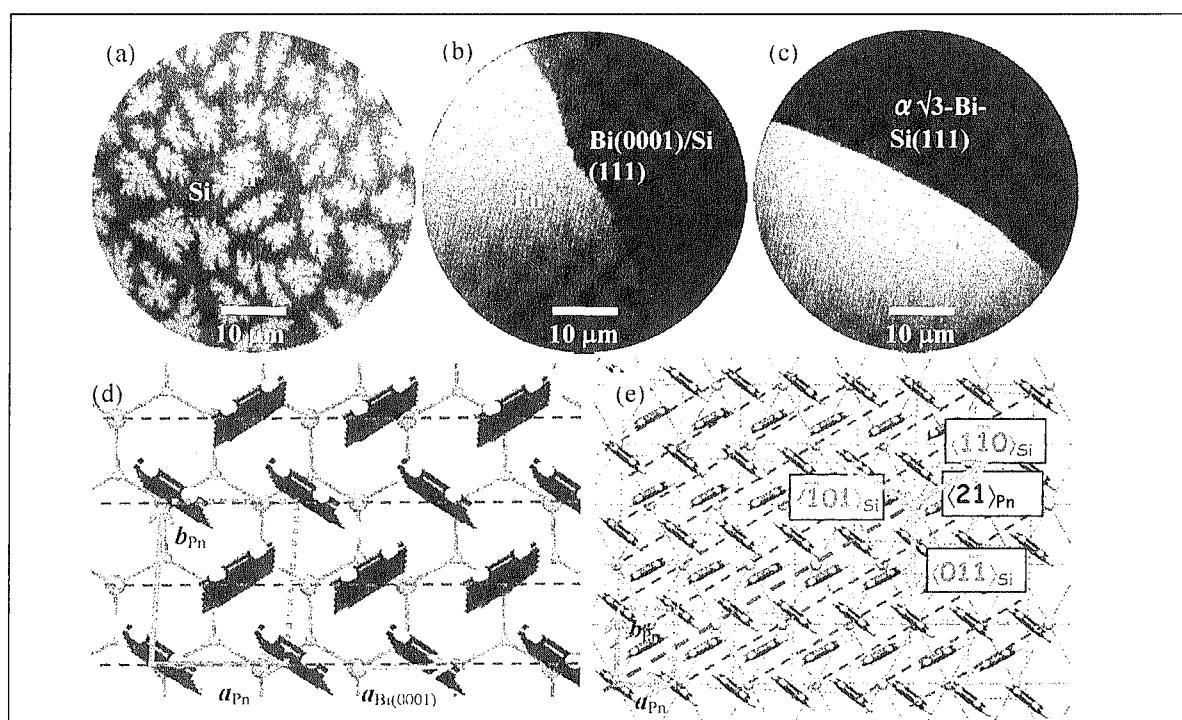
# 論文內容要旨

The mechanism of nucleation and thin film growth of pentacene ( $C_{22}H_{14}$ , Pn) and 6,13-pentacenequinone ( $C_{22}H_{12}O_2$ , PnQ) on silicon substrates have been studied *in-situ* by means of real-time low-energy electron microscopy (LEEM) and low-energy electron diffraction (LEED). The molecular-scale morphology of the Pn films was further studied in scanning tunneling microscope (STM). The *ab-initio* density functional theory (DFT) calculations were employed to investigate possible mechanisms for processes observed in the experiments.

## 1. Pentacene

Step-flow growth of (001)-oriented Pn thin films on Bi(0001)/Si(111) and on  $\alpha\sqrt{3}$ -Bi-Si(111) substrates have been observed, resulting in formation of large, monolayer-high Pn grains with diameters exceeding hundreds of  $\mu$  m. This is different than Pn growth on Si(111)-7x7 where rough interfacial wetting layer induces diffusion-limited growth of fractal-shaped Pn islands.

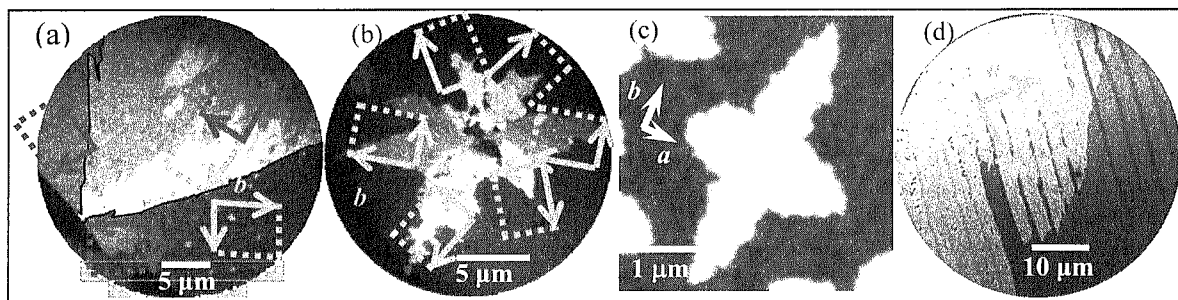
Growth of self-organized Pn films have been stabilized epitaxially on passivated silicon surfaces having large difference in the in-plane lattice parameters, where a self organized Pn polymorph can be stabilized by tuning the electronic property of substrate and a certain level of commensurability could be achieved between the Pn polymorph and the substrates. Point-on-line commensuration (between Pn **a**-axis and one of trigonal substrate's primitive axes) has been observed for a Pn bulk-like polymorph on Bi(0001)/Si(111) surface. A thin film polymorph



**Fig.1.** (a)-(d) LEEM images showing Pn growth (bright contrast) on various substrates (dark contrast): (a) Fractal growth on clean Si(111)-7x7 surface - disordered wetting layer is formed before nucleation of standing-up structure; Pn film is polycrystalline; (b)-(c) Step flow-like growth of compact Pn island on Bi(0001)/Si(111) and  $\alpha\sqrt{3}$ -Bi-Si(111) are observed; The first layer single crystalline domain size are exceeding 200 and 100  $\mu$  m in diameter respectively; (d) Adsorption geometry of Pn on Bi(0001) surface depicted from  $\mu$ -LEED and STM experiments showing point-on-line coincidence between a bulk-like Pn and the substrate: Pn **a**-axis is parallel to one of the substrate primitive vectors and all Pn molecules are lying on primitive lattice lines of the substrate (dashed blue lines); (e) Adsorption geometry of Pn on  $\alpha\sqrt{3}$ -Bi-Si(111) surface showing line-on-line coincidence between a thin film polymorph of Pn and the substrate: pink and dotted lines represent  $\sqrt{3}$ -superstructure and the Pn lattice respectively, dashed blue lines represent the matching direction of lattice lines determined from  $\mu$ -LEED experiments.

of Pn on  $\alpha\sqrt{3}$ -Bi-Si(111) has been epitaxially stabilized with a weak commensuration through a line-on-line coincidence. In this weakly commensurate film, a non-epitaxial twin, having mirror line parallel to in-plane unit cell diagonal direction has been detected, but nevertheless, the twin-free domain region of hundred of  $\mu\text{m}$  in diameter could be realized if the substrate is sufficiently flat and defect-free. Such non-epitaxial twinning was absent in more highly commensurate Pn/Bi(0001) system.

The molecular tilt with respect to surface normal has been found to introduce asymmetry in LEED patterns obtained in LEEM experiments. Utilizing this asymmetry, the presence of chiral epitaxial twins within a domain has been imaged in tilted dark-field imaging mode.

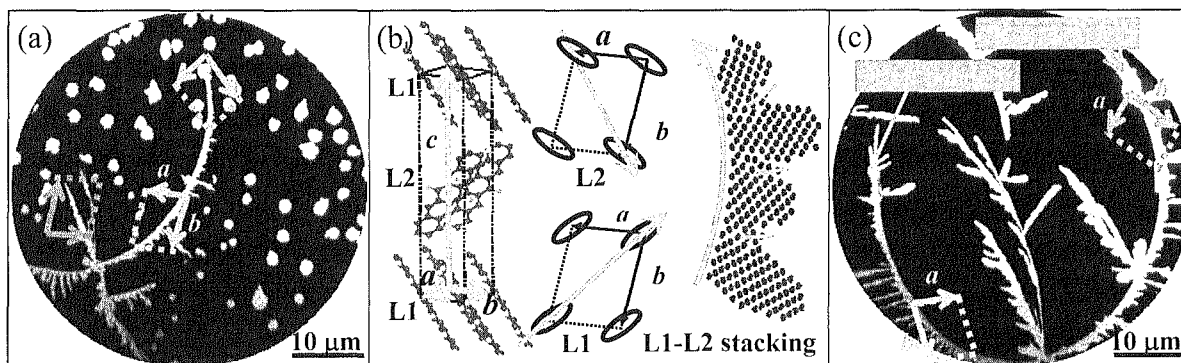


**Fig.2.** LEEM images of Pn domains: (a) Tilted dark-field LEEM image showing rotational Pn domains on trigonal Bi(0001)/Si(111) substrate, additional contrast of chiral twin is visible within a rotational domain; (b) Tilted bright-field LEEM image of the Pn island grown on the H-Si(111) surface, multi-domain structure within an island is visible. 6 domains are nucleated around substrate defect, each domain is directed along their  $b$  directions; (c) Bright-field LEEM image of the 2<sup>nd</sup> layer Pn island on  $\alpha\sqrt{3}$ -Bi-Si(111), the island is elongated along  $\langle 01 \rangle$  direction; (d) Pn (bright contrast) on self patterned Bi(0001) substrate (grey contrast), separated by disordered Bi (0112) region (dark contrast) which limits Pn molecule's diffusion across it (dark contrast), having Pn  $b$ -axis closely parallel to strip direction over the surface within the limit of epitaxial relation; Outlined is the unit cell orientations depicted from  $\mu$ -LEED patterns.

## 2. 6,13-pentacenequinone

In growth of PnQ on Si(111)- $7\times 7$ , the formation of a wetting layer was followed by subsequent nucleation of amorphous and crystalline thin film phase respectively. Amorphous islands grew in an isotropic compact shape. After the compact island grew big enough - typically a few hundreds to several thousands nanometers in diameters - crystalline island nucleated on the top of compact island by a phase transition or by stabilizing a critical island, growth mode of which is highly anisotropic. Anisotropic mass transport from compact to crystalline islands has been observed. The in-plane crystal structure and molecular packing in thin film were determined.

It has been found that the long edge of anisotropic islands aligns along the direction of easier molecule incorporation or lowest kink formation energy at the first PnQ layer, rather than along the lowest-energy step. It has also been observed that molecular tilt of PnQ in surface plane introduces surface chirality in PnQ films. The real-time LEEM study revealed that kinetically stiff direction during film growth differs from the thermodynamic one. This feature together with the asymmetric mass incorporation associated with molecular tilt with respect to surface normal and bond anisotropy results in chiral evolution of PnQ islands. This observation can help to understand the principles of chiral bio-crystallization.



**Fig.3.** (a) LEEM image showing compact (type-I, amorphous) and needle like (type-II, crystalline) PnQ islands (bright contrast) grown on Si(111)-7x7 surface (dark contrast): Type-II islands nucleate on compact island and grow preferentially either along long diagonal,  $\langle \mathbf{a}+\mathbf{b} \rangle$  (unit cell orientation depicted from  $\mu$ -LEED patterns are outlined by red arrows), or short diagonal,  $\langle \mathbf{a}-\mathbf{b} \rangle$  (unit cell orientation is outlined by green arrows): gradual rotation of growth tip is observed which is associated with crystalline orientation (depicted from  $\mu$ -LEED data) of the branch locally growing along  $\langle -\mathbf{a}-\mathbf{b} \rangle$  direction: (b) (left) Outline of thin film PnQ unit cell: a bilayer structure with molecules in alternate layers L1 and L2 in herringbone arrangement: (middle and right) Schematic presentation of a kinetic growth model of ring-like chiral island: preferential growth directions in the L1 (bottom layer) and L2 (alternate layer) of the PnQ film are indicated by red arrows: the gradual rotation of growth tip of an island having L1-L2 stacking is represented by curved arrow at the right image, asymmetric molecule incorporation at the convex side produces additional partial rows of molecules at this side: red lines schematically mark the inclusions of extra molecular rows: (c) LEEM image of a PnQ island showing chiral evolution of ring-like type-II island, branches and its enantiomorph.

## 論文審査の結果の要旨

Al-Mahboob Abdullah氏の論文は、低速電子顕微鏡(LEEM)等の新しい手法を導入し、異方性の高い有機薄膜の結晶構造と無機結晶基板との整合関係と、その異方性がもたらす成長速度の方位依存性を詳細に研究し、有機-無機ヘテロ構造の成長の理解を目指している。

無機結晶基板との整合性については、Si(111)表面をビスマスで修飾することによって作成したビスマス薄膜表面、およびビスマス $\sqrt{3}$ 構造の2つの異なる表面に対するペンタセンの薄膜成長において、薄膜の結晶構造およびその基板構造との整合性を論じており、その結果は異方性の高い結晶構造を持つ有機薄膜と等方的な基板構造との間の整合性と結合の強さが、薄膜成長を理解する上で重要である事を示している。

ペンタセンの成長速度の異方性については、速度論的な結晶成長条件下において、ペンタセンが特定の軸方向に優先して成長する性質を持っており、さらに多くの基板表面において、ドメイン側面で形成された微小核のうち、外部の拡散過程に対して優先成長方向が適合したものが優先的に成長して、単一グレイン内でペンタセン薄膜の多結晶化が起こる事を見いだした。1次元的なパターンを持つ成長基板上で拡散過程を制御することにより、優先成長方向を固定して単結晶を成長する事も示している。この結果は異方性の高い結晶構造を持つ材料の薄膜成長全般において、多結晶化が誘起される機構を明らかにし、成長基板上の拡散制御によって多結晶化が抑制出来る事を示した点において重要である。

ペンタセンキノンの結晶成長においてもLEEM観察を行い、理論的な解析結果を加えて論じている。その結果、その優先成長方向が、最下層のステップにおけるキンク生成エネルギーの異方性に依って説明されることを示した。この結果は有機薄膜成長におけるキンク生成エネルギーの重要性を、実験・理論の両面から示したものと評価できる。

以上の成果は、有機-無機ヘテロ構造の薄膜成長一般に通ずる物理を解明した新規かつ有意義なものである。また、口頭発表においても、筋道立った明確な説明がなされ、質問に対しても大半は的確に答えていた。これらを総合して判断した結果、本人自身が今後自立して研究活動を行うに必要な高度な研究能力と学識を有することを示している。したがって、Al-Mahboob Abdullah提出の論文は、博士(理学)の学位論文として合格と認める。